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A KINETIC STUDY OF THE OXIDATION OF SPHALERITE*

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ABSTRACT

Oxidation of sphalerite has been found to be linear over the range 700 to 830°C with an activation energy of 63.4 kcal/mole. Oxygen concentration--rate studies revealed primary Langmuir adsorption of oxygen prior to thermal decomposition. A reaction mechanism has been proposed for the overall reaction $2 \text{ZnS} + 3 \text{O}_2 \rightarrow 2 \text{ZnO} + 2 \text{SO}_2$ involving single site adsorption of oxygen on sphalerite. On this basis excellent agreement has been obtained between the experimental results and theoretical calculations. The enthalpy of adsorption of oxygen on the surface of the sphalerite was found to be -59.6 kcal/mole. Data are presented which indicate conditions under which either a sulfatizing or an oxidizing roast may be obtained.

INTRODUCTION

Roasting processes have been employed in the metallurgy of a great number of basic metals in use today. Until recently, however, little attempt has been made to deduce the fundamental mechanism by which oxidation takes place. Structural changes upon oxidation have been investigated^(1,2) and thorough work has been performed with regards to the reaction products and the thermodynamics of the oxidation reactions.⁽³⁻⁷⁾ The objective of this investigation was to determine the rate of oxidation of sphalerite and to apply the absolute reaction rate theory in the theoretical interpretation of the experimental results.^(8,9)

DESCRIPTION OF APPARATUS

The apparatus pictured in Figures 1 and 2 contains the following features: (1) furnace with gas system (2) autographic weighing system, and (3) temperature control system.

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7547 02

Figure 1. Front View of Apparatus.

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LIGHT SOURCE

FIGURE 2. BACK VIEW OF APPARATUS.

(1) The furnace was mounted by a yoke on each end and was free to travel up and down on steel guide rods, permitting the introduction and removal of samples from the apparatus with minimum difficulty. The furnace was heated by three sections of Kanthal wire wound externally on a zirconia tube, and insulated with Fiberfrax. Pure gases or mixtures of gases were introduced into the lower end of the furnace through two flow-meters, a mixing chamber, and a gas-tight sparger (Figure 3). The gaseous products of the reaction and the unused gases were prevented from escaping to the atmosphere by maintaining a small negative pressure on the system. This procedure permitted air from the outside to enter through the small annulus around the quartz suspension fiber and prevented the escape of the internal gases.

(2) The autographic weighing system consisted of an adapted gold balance, a photoelectric circuit and a weight recorder (Figure 4). The sample was suspended from one end of the balance beam by means of a platinum chain outside the furnace and a long thin quartz fiber on the inside of the furnace. On the other end of the balance beam, the necessary weights were added to counter balance the sample. In addition, a calibrated chain was added to the balance which was linked directly to the weight recording unit. Control was effected by means of a photoelectric circuit.⁽⁴⁰⁾ A parallel beam of light from a strong source was directed onto a small front-surfaced aluminum mirror mounted in the middle of the balance beam, and then to a front-surfaced mirror mounted on the ceiling of the room. The beam was then reflected onto a front-surfaced right prism at a distance of 9 feet from the balance beam. The right prism which splits the light beam, was located in the cabinet next to the balance. The split beams were directed to the two photo-cells. A slight displacement of the balance beam caused the light to be directed primarily onto one of the two photocells. The impulse thus received was amplified and directed to a shaded-pole motor which drove the recorder pen in the recording unit in the proper direction. At the same time the motor adjusted the gold chain attached to the balance beam, restoring it to a null position. Displacement of the balance beam in the other direction caused the reverse to happen. In this manner, weighing by swings was effected. The change of weight of the sample was recorded continuously on a chart moving at constant speed.

The extent of the swing of the balance corresponded to a line on the moving chart of approximately 0.1 inches (1.3 mg). The rate of movement of the chart was $\frac{1}{4}$ inch per minute, setting the lower limit of rate determination at about 3 mg per hour.

Fig. 3. SCHEMATIC GAS CONTROL AND COLLECTION SYSTEM

Fig. 4. SCHEMATIC DIAGRAM AUTOGRAPHIC BALANCE

(3) The furnace temperature was measured by three chromel-alumel thermocouples located in the tube wall of the furnace approximately in the middle of each winding. The furnace temperature was controlled by the thermocouple located directly against the middle winding of the furnace, operating through a Leeds and Northrup Micromax Type S temperature controlling recorder, a Micromax Electronic Control Unit (MEC) and a Motor Drive Unit (MDU). The power input to each of the three windings of the furnace was separately adjusted by means of a powerstat. A direct linkage between the powerstat to the middle winding of the furnace and the MDU controlled the temperature in the reaction zone to within $\pm 1^\circ\text{C}$ of control setting. Accurate temperature readings were made by switching the thermocouple leads to a type 8662 Leeds and Northrup potentiometer.

EXPERIMENTAL PROCEDURE

The sphalerite samples were cut from massive single crystals of the naturally occurring mineral. For this purpose a jig was constructed on which the sphalerite samples were ground. The samples were ground to shape as nearly as possible along the natural dodecahedral cleavage planes of the sphalerite using a carborundum wheel. The shape of the samples was rectangular—approximately 0.52 inches long, 0.12 inches wide, and 0.055 inches thick. Plate-like samples were used to minimize the change in surface area during oxidation. Samples of these dimensions weighed approximately 0.85 grams. A small hole was drilled at one end of the sample for the purpose of suspension on a quartz fiber inside the furnace. Each sample was cleaned with a washing of dilute hydrochloric acid, two washings of distilled water, and a final wash in alcohol. The sample was then dried and placed on the hook of the quartz fiber and the furnace was slowly lowered over it. Considerable difficulty was experienced in getting the samples into the reaction zone. Since a temperature gradient existed along the furnace tube from the bottom to the reaction zone, thermal stresses were set up in the sample, causing fracture. This resulted in a loss of about 3 samples in every 4. The sample was suspended in pure dry nitrogen while the autographic weighing mechanism was set in operation. The concentration of oxygen was then adjusted to the desired flow rate and a complete rate curve was obtained. The product gases including SO_2 were collected in a three necked flask and titrated with a standard iodine solution to determine the rate of SO_2 evolution.

The dimensions of the samples were carefully measured beforehand, and the sample area calculated. In order to obtain quantitative data, the rate curves were plotted as weight loss per unit area versus time. Corrections were also made for the reduction in area during oxidation.

RESULTS

Typical rate curves obtained in these studies are presented in Figure 5. The oxide formed was very porous and the oxidation rate was found to be linear throughout the temperature range investigated. Also included in Figure 5 at a temperature of 799°C are data before and after correction for the variation in surface area. Although this correction was small it was often significant. It was calculated assuming oxidation occurred evenly at every face of the sample.

The results of 47 separate rate curves are presented in Figures 6 and 7. Figure 6 is a typical rate-temperature plot in which $\log \text{Rate}/T$ is plotted versus $1/T$. These data were obtained in pure, water-free oxygen. The heat of activation under these conditions was found to be 61.7 kilocalories per mole.

To determine the effect of oxygen at low partial pressures a series of rate isotherms were obtained at four different temperatures. The partial pressure of oxygen was varied by dilution with nitrogen. The results of these studies are presented in Figure 7. At low O_2 partial pressures the rate decreased rapidly, falling to zero in pure N_2 . The order of the oxygen concentration-rate curves is typical of an exothermic surface reaction involving an adsorption process.

DISCUSSION

Partial pressure effects as evidenced in Figure 7 resulted in a dependency similar to the Langmuir adsorption isotherm. A definite maximum rate was reached at any given temperature as the partial pressure of oxygen was increased. This suggests a preliminary adsorption process followed by decomposition of surface sites. The concentration of surface sites contributes to the absolute rate of reaction which becomes constant as the fraction of the number of reactive surface sites covered, to the total number of reactive sites available approaches unity.

According to the absolute reaction rate theory,^(8,9)

$$\text{Rate} = \mathcal{P} \frac{kT}{h} \prod_i C_i e^{-\frac{\Delta F^\ddagger}{RT}} = \prod_i C_i k' \quad (1)$$

where $\prod_i C_i$ is the product of the concentrations of the reactants, $\Delta F^\ddagger$ is the free energy of activation, $\mathcal{P}$ is the transmission coefficient,

Fig. 5 Oxidation Rates of Sphalerite in O₂ at Atm. Pressure

Fig. 6. Arrhenius Plot of the Experimental Oxidation Rates of Sphalerite in Oxygen

Fig. 7. Oxidation Rate of Sphalerite versus Oxygen Concentration

Fig. 8. OXIDATION RATE OF SPHALERITE versus O₂ CONCENTRATION

k and h are the Boltzmann and Planck constants respectively, and k' is the specific reaction rate constant. For the thermal decomposition of a surface site containing an adsorbed molecule equation (1) becomes

$$\text{Rate} = k_0 \theta k' = K_0 \theta \quad (2)$$

where θ represents the fraction of the available surface covered with adsorbed oxygen, and k_0 includes the surface roughness factor and conversion units from the fraction of surface covered to true surface concentration.

The adsorption reaction appears to be extremely rapid in this case whereupon it may be considered as an equilibrium process. This may be represented by the equation

from which

$$K_1 = \frac{\theta}{1-\theta} \frac{1}{[\text{O}_2]} = e^{-\frac{\Delta F_1}{RT}} \quad (4)$$

where θ represents the fraction of the surface covered with adsorbed oxygen, K_1 is the equilibrium constant of the adsorption process, $[\text{O}_2]$ is the concentration of oxygen in the gas phase, and ΔF_1 is the free energy of adsorption. Solving for θ results in the typical Langmuir equation

$$\theta = \frac{K_1 [\text{O}_2]}{1 + K_1 [\text{O}_2]} \quad (5)$$

and equation (2) becomes

$$\text{Rate} = K_0 \left[\frac{K_1 [\text{O}_2]}{1 + K_1 [\text{O}_2]} \right] \quad (6)$$

where K_0 is constant at constant temperature. Equation (6) was found to fit the experimental data very closely. The theoretical curves resulting from the evaluation of Equation (6) using two points from each isotherm are plotted in Figures 8 and 9. Attempts were also made to fit the experimental data by other adsorption processes such as the splitting of an oxygen molecule between two surface sites. This would result in a one-half power dependency in terms of oxygen concentration.

Fig. 9 OXIDATION RATE OF SPHALERITE versus O₂ CONCENTRATION

Fig. 10. Relationship of the Equilibrium Constant of Adsorption and Temperature

7547 12

Similarly, reactions involving more than one surface site were investigated. None of these attempts satisfied the experimental data except that requiring single-site adsorption of O_2 . The values of K_1 were determined for each isotherm and are presented in Table I. The variation of K_1 with temperature permits one to evaluate both ΔH_1 , and ΔS_1 , of adsorption since

$$\ln K_1 = -\frac{\Delta F_1}{RT} = -\frac{\Delta H_1}{R} \left(\frac{1}{T}\right) + \frac{\Delta S_1}{R} \quad (7)$$

Figure 10 represents a plot of $\log K_1$ versus $\left(\frac{1}{T}\right)$ for the data of Table I.

TABLE I

$\log K_1$	$T(^{\circ}K)$
4.4	1006
4.004	1033
3.580	1066
3.236	1092

From the slope of the line ΔH_1 was found to be -59.6 kilocalories per mole. The magnitude of ΔH_1 indicates chemisorption of O_2 . The value of ΔS_1 was determined from Equation (7) and was found to be -39.2 e.u.

The over all reaction

may be considered as a series of separate steps involving the adsorption of O_2 . The end products ZnO and SO_2 have been shown to form under the conditions of these studies. Following chemisorption of O_2 as represented by Equation (3), the surface may decompose as follows:

and

ultimately resulting in the formation of ZnO and SO_2 . The postulation of the existence of SO as an intermediate product has been suggested before.^(11,12,13) Its presence would be only transitory and would be immediately removed by reaction (10).

Fig. 11. TOTAL ABSOLUTE RATE OF REACTION OF SPHALERITE
IN OXYGEN versus RECIPROCAL TEMPERATURE

Fig.12 Rate of Zinc Sulfate Formation from
ZnO in various gases at 780°C.

According to Equation (9) which represents the rate determining step

$$\text{Rate} = \rho \frac{kT}{h} k_o \theta e^{-\frac{\Delta H^\ddagger}{RT}} e^{-\frac{\Delta S^\ddagger}{R}} \quad (11)$$

A plot of $\ln \text{Rate}/\theta T$ versus $1/T$ should correlate all of the data including those runs with oxygen present in low concentrations. These results are plotted in Figure 11 showing the correlation between experiment and the proposed mechanism. The heat of activation, $\Delta H^\ddagger$, was found to be 63.4 kilocalories per mole.

If the rate of the reaction is measured in molecules/cm² sec., k_o of Equation (11) has the units, molecules/cm². It is interesting to determine its value in terms of the proposed mechanism. Consistent with the proposed rate controlling reaction, Equation (9), $\Delta S^\ddagger$ should be very small. Assuming its value to be zero, k_o determined under the conditions $T = 1072^\circ K$, rate = 17.86 mg./cm²hr., and $\theta = 0.968$, was found to be 1×10^{12} molecules/cm². Along the natural dodecahedral cleavage planes of sphalerite there are approximately 4.8×10^{14} surface sites per square cm. This does not account for surface roughness, but the agreement is sufficiently close to indicate that nearly every surface Zn-S site is an adsorption site.

SULFATE FORMATION

Throughout these studies both weight changes and SO₂ evolution were measured. In all cases the amount of ZnSO₄ formed was found to be negligible. A final experiment was performed in which a plate of pure zinc oxide was reacted with pure SO₂ and then a mixture of SO₂ and O₂ at a temperature of 780°C. A plate 22 mm. in diameter and 1 mm thick was prepared by pressing analytic grade ZnO in an evacuated die using a 20 ton load. The results are shown in Figure 12 where weight gain is plotted versus time. The region a to b shows no weight gain during the time that N₂ was passed over the sample. After 20 minutes SO₂ by itself was passed over the sample (b to c). No weight change occurred in the presence of SO₂ alone. Next, a stoichiometric quantity of O₂ for sulfate formation was added with SO₂. A rapid weight gain was noticed and is shown in Figure 12 c to d. At d the SO₂ was shut off and in the presence of O₂ alone the sample lost weight immediately. The ZnSO₄ formed decomposed very rapidly and at time e the sample was removed from the furnace. The sample was extracted soon enough that all

of the $ZnSO_4$ had not decomposed. The weight gain of the sample was compared with the amount of sulfate in the sample determined by conventional quantitative techniques and found to correspond closely with the observed weight gain.

Data reported by Maier⁽¹⁴⁾ from the equilibrium data of Wöhler, Plüddemann and Wöhler⁽¹⁵⁾ showed that the equilibrium SO_3 partial pressure for the $ZnSO_4-SO_3$ system at $775^\circ C$ is 1.96×10^{-2} atmospheres SO_3 . It may be concluded that sulfate formation is subsequent to the formation of ZnO and its formation requires the presence of both SO_2 and O_2 . The type of roast product formed, either sulfatizing or oxidizing, may thus be controlled by the relative quantities of SO_2 and O_2 present. Additional studies are being carried out in this laboratory to determine the kinetics of sulfate formation.

SUMMARY

(1) The oxidation of sphalerite has been found to be linear over the range $700^\circ C$ to $830^\circ C$, with an activation energy of 63.4 kcal/mole.

(2) Studies of the rate as a function of oxygen concentration have indicated primary single-site adsorption of oxygen on the surface with an enthalpy of adsorption of -59.6 kcal/mole and -39.3 cal/deg. mole respectively.

(3) In the light of the experimental evidence presented, the over-all reaction $2 ZnS + 3 O_2 \rightarrow 2 ZnO + 2 SO_2$ has been postulated to occur according to the following steps:

(a) $ZnS + O_2 \rightleftharpoons ZnS[O_2]$ (equilibrium chemisorption)

(b) $ZnS[O_2] \rightarrow$ activated state $\rightarrow ZnO + SO$ (rate determining)

(c) $2 SO + O_2 \rightarrow 2 SO_2$ (fast).

(4) An investigation of the possibility of sulfate formation has indicated that a negligible amount of sulfate is formed during the roasting of sphalerite.

(5) Conditions have been proposed however, under which either a sulfatizing roast or an oxidizing roast may be obtained by maintaining the SO_2 concentration in the roast above a certain specified amount.

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12
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